Air Analysis Using Tenax Collection with Jet-Separator Enrichment and Ion Trap Mass Spectrometric Analysis

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A dual adsorbent trap inlet system has been developed for an ion trap mass spectrometer (ITMS) to provide a rapid and sensitive system for screening of volatile organic compounds in air. The system employs three stages of concentration: preconcentration on an adsorbent Tenax trap, focusing in a cryogenic collection trap, and jet separator enrichment immediately prior to analysis by ITMS. Ten minute integrated samples are collected and analyzed immediately. The detection limit is 0.9 parts-per-trillion by volume (pptrv) based on toluene as the analyte, and the reproducibility is 2% or better. Ambient air was analyzed for toluene on April 4, 1996 in Los Alamos, New Mexico, and concentrations ranged from 11–158 pptrv.
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In this article we describe an air analysis system that uses Tenax collection of volatile organic compounds (VOCs) from air, followed by cryogenic focusing and enrichment with a jet separator for analysis by quadrupole ion trap mass spectrometry. Rapid methods of air monitoring for VOCs are becoming increasingly important for understanding tropospheric ozone production, emission control, and indoor air quality [1]. Several mass spectrometric methods have been reported that are suitable for such analyses. Atmospheric pressure ionization (API) coupled with tandem mass spectrometry has been used for the real-time analysis of atmospheric pollutants [2, 3]. This technique demonstrates very high sensitivity in many cases, but the API mechanism can suffer from matrix effects [4, 5] and interferences from ion-molecule reactions. The instrumentation is complex. A methodology that shares the high sensitivity of API/MS is atmospheric sampling glow discharge ion trap mass spectrometry [6]. An advantage of this technique compared to more conventional ion trap methods is the use of external ionization which facilitates negative chemical ionization (NCI) with the ion trap mass spectrometer; impressively high sensitivities have been demonstrated for nitroaromatic compounds using electron capture NCI [6]. Direct sampling ion trap mass spectrometry (DSITMS) [7] and membrane introduction mass spectrometry (MIMS) [8] use simpler instrumentation and can be used for the analysis of many sample types, including soils and water. DSITMS can be applied to a wide range of compounds, including semi-volatile organic compounds; detection limits are about 1 part-per-billion by volume (ppbv) and the linear dynamic range is 10^3. Detection limits to low parts-per-trillion by volume (pptrv) levels with linear response over 4 decades of concentration for air [9] and parts-per-quadrillion levels for water [10] have been demonstrated with MIMS.

Solid adsorbent sampling is a widely used technique for preconcentrating VOCs in air samples [11, 12]. These adsorbents have the ability to collect large volumes of hydrocarbons, while rejecting interfering species such as water vapor and oxygen [13]. Tenax porous polymer [poly(p-2,6-diphenylene oxide)] is one of the most popular adsorbents for the collection of hydrocarbons greater than C_2. It has been evaluated extensively for its ability to collect and release adsorbed hydrocarbons [14, 15]. A wide variety of other solid adsorbents are available and can be selected to trap species as volatile as C_2 compounds. Releasing the trapped hydrocarbons from porous polymers is accomplished by heating for several minutes at 200–300 °C under a flow of inert gas [16]. Because the hydrocarbons are released over a period of several minutes, a secondary collection or focusing step is necessary. Cryogenic collection traps are ideal for this application, as they are uncomplicated devices that can be heated rapidly to release the hydrocarbons. We have com-

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bined this sampling technology with a jet separator between the collection trap and the ion trap mass spectrometer; the jet separator reduces throughput of low molecular weight gases such as helium purge gas and water vapor and provides another enrichment step, as has been previously demonstrated with membrane interfaces for mass spectrometry [17].

The technique presented in this article, solid adsorbent preconcentration of VOCs in air samples, followed by cryogenic focusing and jet separator enrichment prior to the ITD analysis of the VOCs, parallels the MIMS technique, which is applicable to aqueous and air samples. There are three advantages of the technique presented here in contrast to MIMS for air analysis. The first is a tenfold increase in sensitivity. The second is the wide range of compounds that can be detected with fairly uniform response factors. Although techniques to extend MIMS to other compound classes such as polar VOCs have been described [18], the relative sensitivity to MIMS to different compounds can vary by orders of magnitude. The third advantage is the ability to tailor compound collection by use of specific adsorbents. Although chemically modified membranes that can selectively adsorb specific analytes in aqueous solutions have been demonstrated [19], it is likely that parallel techniques will be less applicable to air analysis. The adsorbent technology, on which the technique presented here is based, has been well developed for gas chromatography, and can be readily adapted while selective membrane technology for MIMS is still in its infancy.

Experimental

Ion Trap Mass Spectrometry System

Figure 1 details the sampling and analysis system used for determination of VOCs in air. A modified Finnigan Model 800 ion trap detector (ITD) is utilized with a Finnigan ITS-40 electrode assembly. In this electrode assembly, the endcap electrodes are isolated from ground so that ac potential can be applied for resonant excitation experiments. A sine wave (500 kHz, ~ 6 V_{p-p}) was applied to one endcap electrode (keeping the other endcap grounded) for resonant ejection of the trapped ions as previously described [9]. Although this method of implementing axial modulation is different than the conventional method where the ac is applied differentially to the two endcap electrodes, the overall benefits are the same: sensitivity, dynamic range, and mass resolution are all improved [20]. Version 4.1 of the Finnigan Ion Trap Detector software was used with the automatic gain control option. Full scan mass spectra were acquired at the rate of one per second; each mass spectrum was the average of 9 microscans.

A metal (stainless steel) jet separator (P/N 113617, SGE, Inc., Austin, TX), pumped by a 413 L/min mechanical vacuum pump (Model 2021, Acatel Vacuum Products, Hingham, MA), is connected between the sampling system and the ITD. The flow rate is adjusted so that no additional He was required as a buffer gas in the ITD. The jet separator is maintained at a temperature of 150 °C with heating tape, and the ITD manifold is heated to 260 °C.

Tenax Collection and Preconcentration System

The sampling and analysis system is comprised of a dual Tenax trapping system followed by a cryogenic collection loop (Figure 1). In this dual trap system, one of the adsorbent traps is collecting VOCs while the other trap is being desorbed into the cryogenic focusing loop. Similar dual trapping systems are used in applications for sampling atmospheric tracers [21].

The air sample is directed through one of the two adsorbent traps by the 10 port valve V_1 (P/N

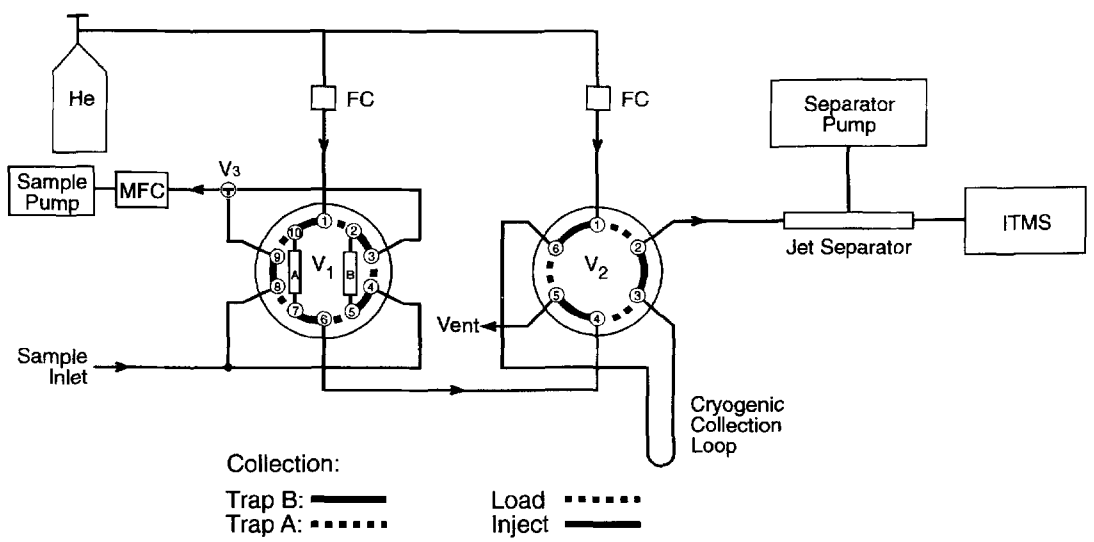

Figure 1. Schematic diagram of the combined dual trap/jet separator ITMS system for the analysis of VOCs in air. FC represents a mechanical flow controller; MFC is an electronic mass flow controller.

E410UWE, Valco, Houston, TX) and the three-way solenoid valve V_3. V_1 is maintained at 50 °C. The sample air flow through the adsorbent trap is regulated at 250 sccm (standard cubic centimeters per minute) by an electronic mass flow controller (FC-260v, Tylan General, San Diego, CA). The adsorbent traps are constructed from a 10 cm length of 6.4 mm o.d. × 0.6 mm wall Silcosteel tubing, coated with a fused silica lining to reduce adsorption on the walls. Approximately 0.33 g of 60/80 Tenax TA (Alltech, Deerfield, IL) is used in each trap. The Tenax is preconditioned before initial use by heating to 150 °C for 1 h and then 300 °C for 2 h under a 30 sccm He flow.

A six port valve V_2 (P/N D6UWE, Valco) controls the loading of the VOCs onto the cryofocusing loop. This loop is constructed from 25 cm of 3.2 mm o.d. × 2.2 mm i.d. stainless steel tubing and filled with 0.28 g of 60/80 dimethylchlorosilane-treated glass beads. This valve is temperature regulated at 100 °C.

The collection and analysis sequence is designed around a 10 min cycle, comprised of four periods. After the completion of the sampling cycle for trap A, V_1 and V_3 switch so that trap A can be desorbed with trap B in the collection mode. The He carrier flows through the trap A for 2 min, which is still at room temperature, to flush the air and water vapor out of the trap before it is heated. After the 2 min flush period, trap A is heated to 200 °C for 4 min, with the He still flowing, and the collected VOCs are back flushed off the Tenax. At the instant the heating is initialized, V_2 switches to the LOAD position to place the cryogenic collection loop in the exit flow from V_2 and the collection loop is immersed in 5 cm of liquid nitrogen (LN_2). On completion of the 4 min desorb period, the LN_2 is removed from the loop, V_2 switches to the INJECT mode, and the ITD data acquisition is started. Ten seconds later the cryogenic loop is resistively heated by applying 25 A at 6 VAC directly to the loop. The loop is heated from liquid nitrogen temperature to 200 °C in 6.5 s. The temperature of the loop is monitored by a thermocouple silver soldered to the bottom of the loop. The VOCs are flushed out of the cryogenic loop in a few seconds once the loop temperature reaches 200 °C. Temperature regulation is not required. The Tenax trap is allowed to air cool for two minutes before being cooled by liquid CO_2 cryogen to speed cooling to room temperature for the next collection cycle.

Ultrapure helium, regulated by mechanical flow controllers FC1 and FC2 (SC440FC, Veriflow, Richmond, CA), is used as the carrier gas to sweep desorbed VOCs through the cryogenic collection loop into the ITD. The He flow rate through the Tenax traps is 30 sccm, and 15 sccm is used to carry the contents of the cryogenic loop into the ITD.

Gas phase VOC calibration standards were generated from permeation tube or permeation wafer sources (VICI Metronics, Santa Clara, CA) held at constant temperature in a heated circulating water bath. Compressed ultrapure air (Scott-Marrin, Riverside, CA) was regulated by electronic mass flow controllers over the permeation devices. The flow rate over the permeation source was 20 sccm, and the dilution flow was varied to obtain a range of concentrations.

Table 1. Summary of analytical system

Compound	m/z measured	Detection limit[a] (pptrv)	Reproducibility[b]
Toluene	91	0.9	1.4, 1.9, 2.0
Trichloroethylene	132	8	1.0, 1.5, 1.5
1,1,1, Trichloroethane	97	90	2.1, 3.3, 3.3
1,1,1, Trichloroethane	99	57	1.4, 3.8, 4.7
Benzene	77	36	0.7, 3.2, 3.7
Benzene	78	16	0.7, 0.8, 0.9

[a] Detection limit is based on 3 times the standard deviation of three blank samples.
[b] Relative standard deviation on three independent runs each based on three consecutive samples.

Results and Discussion

Four different VOCs, toluene, benzene, trichloroethylene and 1,1,1-trichloroethane, were examined on the analytical system for detection limit and analytical reproducibility as defined by the relative standard deviation for three consecutive samples. These results are summarized in Table 1. The lowest detection limit was obtained for toluene at 0.9 pptv, based on three times the standard deviation of three blank samples. Each of the analytes in Table 1 were measured individually.

The linearity performance for toluene is indicated by the calibration curve over the concentration range 15–540 pptrv (Figure 2). Each data point is based on the average of three consecutive samples of the gas phase standard. The error bars in Figure 2 represent one standard deviation. From this calibration, the concentration of toluene can be calculated by $[\text{Toluene}]_{\text{pptrv}} = 0.035 + 2.71\ E = 4$*peak area at m/z 91. The r^2 for six data points, including zero, over the total range is 0.99977.

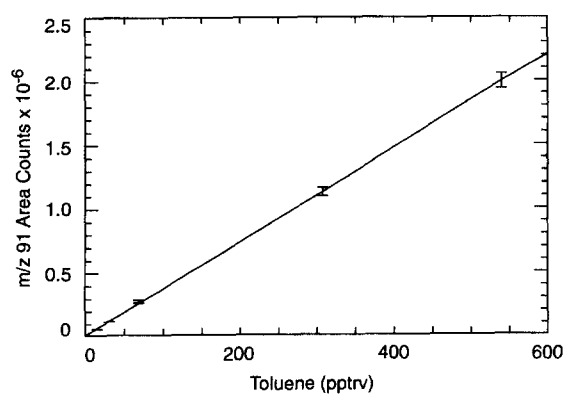

Figure 2. Working calibration curve for the determination of toluene in air over the range 15–540 pptrv.

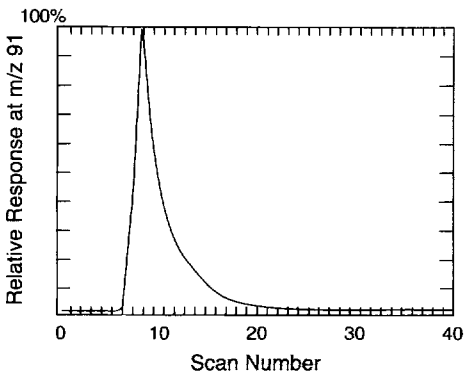

Figure 3. Selected ion current at m/z 91 for a 159 pptrv toluene in air standard acquired at a scan rate of one scan/s. Each scan is comprised of 9 microscans.

Figure 3 shows the response of the system to a standard 150 pptrv sample of toluene. The mass spectrometer is set to acquire data at the time the injection valve, V_2, is switched to the INJECT position, and 10 s later the heat is applied to the cryogenic collection loop. There is a delay of about 9 s for the sample to transfer to the mass spectrometer; mass spectral detection of the desorbed sample occurs in a period of about 2.5 s. Analyte from a 2.5 L air sample (collected over a 10 min period) is ultimately concentrated into a volume of less than 0.5 mL in the cryogenic collection loop, following Tenax preconcentration. This is a concentration factor of about 5000; another substantial stage of enrichment is obtained with the jet separator which removes most of the helium.

Ambient Air Measurements

On April 4, 1996, ambient air measurements for toluene were conducted from Technical Area 46, Building 200, at Los Alamos National Laboratory. This location is on the southeastern edge of the main laboratory complex. The data for the measurements are given in Figure. 4. Atmospheric toluene originates primarily from automobile sources, both fuel evaporation and tailpipe emissions [22–24]. These measurements are toluene equivalents based on m/z 91 as the analytical ion and calibrated as toluene.

The data in Figure 4 shows relatively low concentrations of toluene. A cold front passed through the area in the early morning prior to the start of the sampling. This brought cold, clean air into the region. The wind at the sampling site was from the southwest, and the only source of toluene upwind is the local highway at the laboratory. The concentrations of toluene are in the 20–60 pptrv range during much of the day with no systematic variation. The two samples collected from 17:00–17:20 show a large increase in concentration from the increased vehicle traffic at the end of the work day.

Although other alkyl benzene compounds can produce an ion at m/z 91, toluene is expected to make the

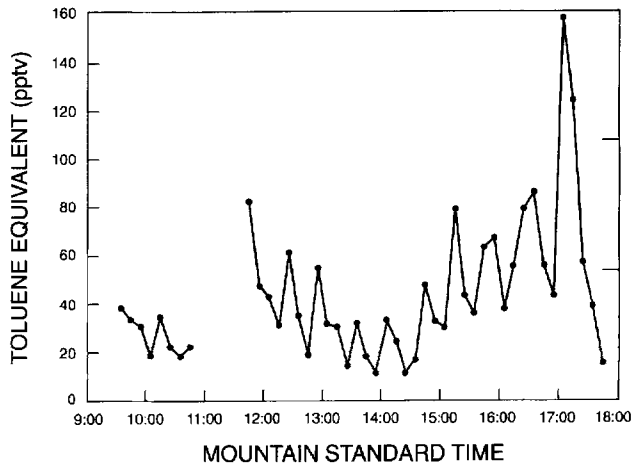

Figure 4. Results from air monitoring experiment on April 4, 1996. Toluene concentrations were measured from 09:30 to 17:50.

major contribution to these measurements [25]. An examination of m/z at 106, 119, 120, and 135, which correspond to larger substituted aromatic compounds, show that an upper limit of 25% of the toluene equivalent from m/z 91 could be attributed to ethylbenzene or xylenes as given by the material measured at m/z 106. No indication could be found for compounds at m/z 119, 120, or 135 contributing to the toluene equivalent concentration.

These measurements are consistent with concentrations expected under these conditions. In remote tropospheric locations, such as the Mauna Loa Observatory in Hawaii, concentrations under 10 pptrv have been measured [26] using cryotrapping for preconcentration and GC-MS analysis of the sample. In rural Alabama, an ambient concentration of toluene was measured as 104 pptrv for an average of 24 samples collected over a one day period [27]. The influence of anthropogenic sources of toluene can be seen by contrasting these remote measurements to those made in urban areas: typical concentrations in Denver have been measured at 19 ppbv [28] and Boston at 4 ppbv [29]. The atmospheric lifetime (1/e) for toluene is estimated at 4.5 h [25], which means it will be removed from the air rapidly. Under the conditions encountered at Los Alamos, the background toluene concentrations would be expected to be low since there are no major urban areas upwind that would be sources of toluene.

Summary

The analytical system demonstrated here can be applied to a wide variety of VOCs in air with minimal changes, primarily in the selection of the adsorbent. The detection limit for species other than toluene would be expected to be similar to that for toluene, because the ITMS, which is the central part of the analytical system, has similar sensitivities for a wide range of compounds. The advantages of this technique, such as high and relatively uniform sensitivity and selectivity

through adsorbent selection, make it an attractive alternative to other on-line mass spectrometric techniques for air analysis such as MIMS and DSITMS.

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